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**TRANSMITTAL OF REPORT ADDRESSING KEY TECHNICAL ISSUE (KTI) ITEMS
EVOLUTION OF THE NEAR-FIELD ENVIRONMENT (ENFE) 2.07 AND 2.08**

This letter transmits a report entitled *Agreements ENFE 2.07 and 2.08* which satisfies the subject KTI agreements. These KTI agreements are as follows:

ENFE 2.07: "Identify specific coupling relationships that are included and excluded from TSPA, including Onsager couples, and give technical bases for their inclusion or exclusion.

DOE will identify specific coupling relationships that are included and excluded from TSPA, including Onsager couples, and give the technical basis for inclusion and exclusion. This information will be documented in a revision to the *Engineered Barrier System Degradation, Flow, and Transport* PMR (TDR-EBS-MD-000006) expected to be available September 2001."

ENFE 2.08: "Provide stronger technical basis for the suppression of individual minerals predicted by equilibrium models.

DOE will provide additional technical basis for suppression of individual minerals predicted by equilibrium models, in a revision to the *Engineered Barrier System: Physical and Chemical Environment Model* (ANL-EBS-MD-000033) expected to be available in FY02."

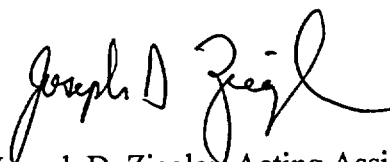
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Agreement Item ENFE 2.07 concerns the coupling effects of the near-field chemical environment within the Engineered Barrier System. A Process Model Report (PMR) was planned to document the information about the various coupling effects. As a result of programmatic changes, PMRs are no longer being developed. Instead, the information needed to satisfy the KTI Agreement Item ENFE 2.07 is provided in this enclosure. The enclosure presents the technical bases for considering the near-field environmental coupling aspects used in Total System Performance Assessment models. Agreement Item ENFE 2.08 concerns the technical bases for the suppression of different minerals that the equilibrium models predict. The enclosure provides a detailed description of the process based on the new version of EQ3/6 (version 8). The geochemical modeling methodology is described to provide the technical basis for the inclusion or exclusion of minerals. The primary reaction path equilibrium model that will be used in the revision to the physical and chemical environment model is developed in the in-drift precipitates/salts model. These models focus on the suppression or inclusion of minerals in the engineered barrier system. The material presented in the enclosure directly addresses the KTI agreement items ENFE 2.07 and 2.08.

The contents of this transmittal were discussed with your staff on September 11 and September 26, 2002, who indicated that ENFE 2.07 should also address the impacts of coupled processes on waste package corrosion. However, consistent with the topical area of ENFE KTI Subissue 2, U.S. Department of Energy (DOE) considers the original scope of both ENFE 2.07 and 2.08 to be related only to the effects of coupled thermal-hydrological-chemical processes on the waste package chemical environment, which is fully addressed by the enclosure. The impacts of the coupled processes, such as corrosion, should be addressed in the appropriate KTI of those processes, such as the Container Life and Source Term KTI for waste package corrosion. Therefore, DOE believes that ENFE 2.07 and 2.8 should be closed.

There are no new regulatory commitments in the body or the enclosure to this letter. Please direct any questions concerning this letter and its enclosure to Timothy C. Gunter at (702) 794-1343 or Deborah L. Barr at (702) 794-1479.



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Enclosure:
Agreements ENFE 2.07 and 2.08

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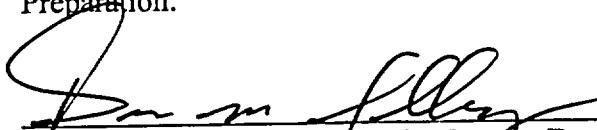
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AGREEMENTS ENFE 2.07 AND 2.08

September 2002

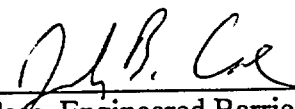
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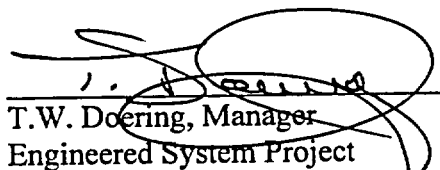

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ENCLOSURE

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ACRONYMS AND ABBREVIATIONS

AMR	Analysis and Model Report
ANC	Acid Neutralizing Capacity
CFR	Code of Federal Regulations
DOE	U.S. Department of Energy
EBS	Engineered Barrier System
ENFE	Evolution of the Near-Field Environment
IDPS	In-Drift Precipitates Salts
IRSR	Issue Resolution Status Report
KTI	Key Technical Issue
LA	License Application
NRC	U.S. Nuclear Regulatory Commission
OCRWM	Office of Civilian Radioactive Waste Management
P&CE	Physical and Chemical Environment
PDE	Partial Differential Equation
RH	Relative Humidity
SR	Site Recommendation
SSPA	Supplemental Science and Performance Analyses
TSPA	Total System Performance Assessment
UZ	Unsaturated Zone
YMP	Yucca Mountain Site Characterization Project

1. AGREEMENTS ENFE 2.07, 2.08

This letter report provides information to address two Key Technical Issue (KTI) agreements related to the evolution of the near-field environment (ENFE) KTI and specifically to the engineered barrier system (EBS) geochemical environment. Each KTI agreement addresses phenomena or considerations related to the EBS geochemical environment in a repository environment and the ability of the U.S. Department of Energy's (DOE) to model these phenomena accurately and adequately.

The information in this letter report is provided in four parts. Part 1 provides the background and summarizes the technical issues of interest to the U.S. Nuclear Regulatory Commission (NRC). Part 2 provides the wording of the agreements and the status of their various component information needs. Part 3 provides the information called for by each KTI agreement, including the technical bases for any assertions and assumptions. Part 4 lists references.

1.1 BACKGROUND FOR AGREEMENTS ENFE 2.07, 2.08

The primary focus of the KTI related to ENFE is the adequacy of the technical basis for the models describing the chemical environment within the EBS in order to demonstrate that there is a reasonable expectation that the models capture the range of expected processes and process interactions. The ENFE KTI is focused on evaluating the adequacy of the methodology, testing, and modeling used by the DOE in the investigations related to the environmental conditions within the engineered and near-field repository environment.

The agreement items were reached during technical exchange meeting on key technical issue and subissues related to evolution of the near-field environment between the NRC and the DOE in January 2001. Agreement items ENFE 2.07 and 2.08 seek information concerning the specific coupling relationships that are included or excluded in the total system performance assessment (TSPA) and the technical basis for the suppression of minerals in chemical equilibrium modeling.

2. APPLICABLE NUCLEAR SAFETY STANDARDS, REQUIREMENTS AND GUIDANCE

10 CFR part 63, Subpart B, provides the requirements for pre-application review. These pre-application reviews include informal conferences between a prospective applicant and the NRC staff, as described in 10 CFR 2.101(a)(1). Consistent with these requirements and in accordance with the memorandum of understanding between the two federal entities, *Agreement between DOE/OCRWM and NRC/NMSS Regarding Prelicensing Interactions* (Barrett et al., 1999), a series of interactions was undertaken to identify information needed for a prospective license application. At these meetings, agreements for the DOE to provide the NRC with information were recorded as KTI agreements.

2.1 APPLICABLE REQUIREMENTS

The Yucca Mountain disposal regulations include requirements to describe the geochemical environment, taking into account uncertainties in characterizing and modeling the behavior. The geochemical descriptions and the technical basis for models are used to support the performance assessment regulations 10 CFR 63.114(a) through (g), and 10 CFR 63.115(c). Agreement items ENFE 2.07 and 2.08 are related to describing the near-field environment within the EBS under various repository conditions. Also, the monitoring and testing of waste package requirements in 10 CFR 63.134(c) are applicable.

2.2 KTI AGREEMENTS

Quoted below are the two ENFE KTI agreements that are the subject of this letter report. The purpose of these agreements is to ensure that sufficient information is available on a given KTI to enable the NRC to docket a license application. Wording of ENFE KTI agreements is based on summary highlights of the technical exchange and management meeting on key technical issues and subissues related to evolution of the near-field environment between the NRC and the DOE on January 2001:

- Identify specific coupling relationships that are included and excluded from TSPA, including Onsager couples, and give technical bases for their inclusion or exclusion. DOE will identify specific coupling relationships that are included and excluded from TSPA, including Onsager couples, and give the technical basis for inclusion and exclusion. This information will be documented in a revision to the Engineered Barrier System Degradation, flow, and Transport PMR (TDR-EBS-MD-000006) expected to be available in FY02 (ENFE 2.07).
- Provide stronger technical basis for the suppression of individual minerals predicted by equilibrium models. DOE will provide additional technical basis for suppression of individual minerals predicted by equilibrium models, in a revision to the Engineered Barrier System: Physical and Chemical Environment Model (ANL-EBS-MD-000033) expected to be available in FY02 (ENFE 2.08).

2.3 STATUS OF AGREEMENTS

Prior to the technical exchange and management meeting on key technical issues and subissues related to evolution of the near-field environment between the NRC and the DOE in January 2001, the five ENFE subissues were considered open. Following the meeting Subissues 1, 2, 3, and 4 were classified as closed-pending. While these subissues remain closed pending at this time, in recent months NRC staff and DOE staff have discussed the work covered under these agreement items and the proposed approach by the DOE to satisfy the intent of the agreements. The DOE has also prioritized the work related to the KTI using a risk-informed approach. DOE presented the risk-informed approach to the NRC during the technical exchange meeting held on April 15-16, 2002. At this meeting, the DOE proposed closing a number of agreement items in fiscal year 2002, including the two agreement items in this report. The technical bases for closing the agreements were to be documented in letter reports sent to the

NRC for review and acceptance. This letter report documents the basis for closure of ENFE agreement items 2.07 and 2.08.

3. INFORMATION TO SATISFY KTI AGREEMENTS

3.1 ENFE 2.07

3.1.1 Introduction

DOE has agreed to identify specific coupling relationships that are included in and excluded from the TSPA model, including Onsager couplings, and to give the technical basis for inclusion and exclusion in KTI agreement ENFE 2.07 with the NRC. This section provides information in support of KTI Agreement 2.07 and for the EBS physical and chemical environment (P&CE) model report to be issued in the future.

Coupled processes in this case refers to processes which depend on two or more physical and chemical variables simultaneously interacting to produce a result. The coupled processes to consider in the TSPA involve transport of chemicals, specifically radionuclides which can affect dose calculations. Onsager couplings are driven indirectly by gradients of thermodynamic state variables (e.g., temperature, pressure, chemical potential, and electrical potential) that affect chemical transport in aqueous solution. Direct transport processes are driven by the same thermodynamic state variables in well-known relations such as Fourier's Law, Darcy's Law, Fick's Laws, and Ohm's Law. Diffusive processes dominate in Onsager-coupled processes and the direct transport processes named above.

Internationally, there is increasingly more interest shown in the relative contributions of specific physical-chemical coupling relationships for processes which have the potential to affect Total System Performance Assessment for proposed repositories for the storage of high level nuclear waste (Zhou et al. 1998; Soler 2001). Most of the other proposed repositories are situated in the saturated zone for which some coupled processes may be different than the unsaturated zone at Yucca Mountain.

Our EBS strategy for investigating the importance of these coupled transport processes is simple and straightforward: (1) spatially identify the areas where chemical transport processes can occur and study only those areas and the processes within them (Section 3.1.2); (2) evaluate the coupled and direct transport processes (dominantly diffusive) (Section 3.1.3) which can occur within those areas and screen any processes out that do not occur because of inappropriate boundary conditions (such as temperature vaporizing almost all macro-forms of liquid water within the drift) (Section 3.1.5); (3) realize that if current models can be well validated without including coupled processes, that traditional scientific hypothesis testing states that the simplest model is sufficient to confirm the hypothesis (Section 3.1.4) and coupled processes are considered a second-order effect, and (4) for the cases where coupled processes cannot be screened out for other reasons, perform quantitative transport calculations which determine whether individual processes are negligible or not for the EBS boundary conditions (Section 3.1.6). In other words, we only investigate coupled processes in areas where they are known, or are suspected, to occur, screen them out if EBS conditions prohibit them from occurring, test them quantitatively where they cannot be screened out, and consider them to be

insignificant second-order effects where simpler models are well validated while neglecting them.

3.1.2 Locations of Liquid Diffusive and Advective Transport Processes in the EBS

To understand where coupled processes are potentially important, it is useful to summarize the location of diffusive and advective transport processes in the EBS (Figures 1 and 2).

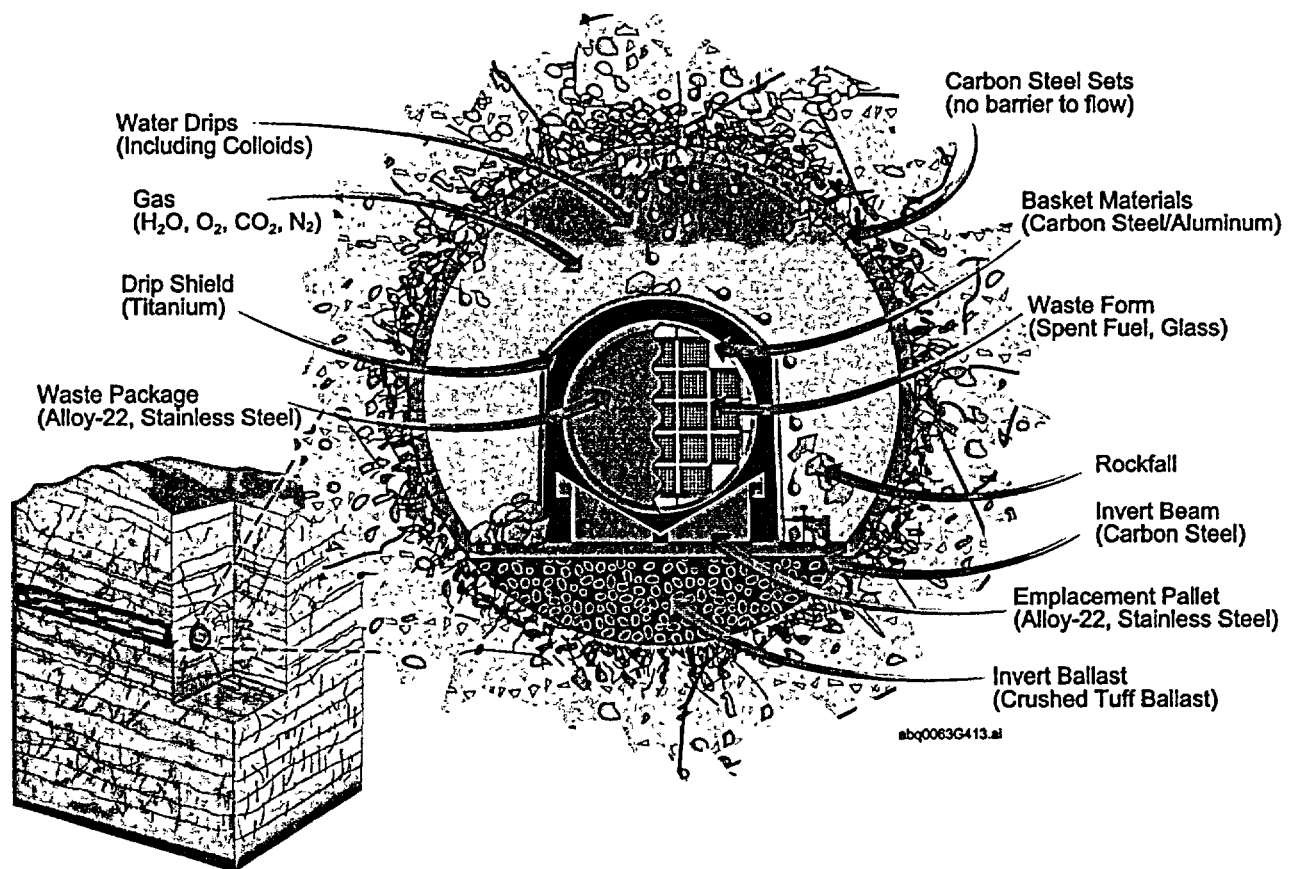
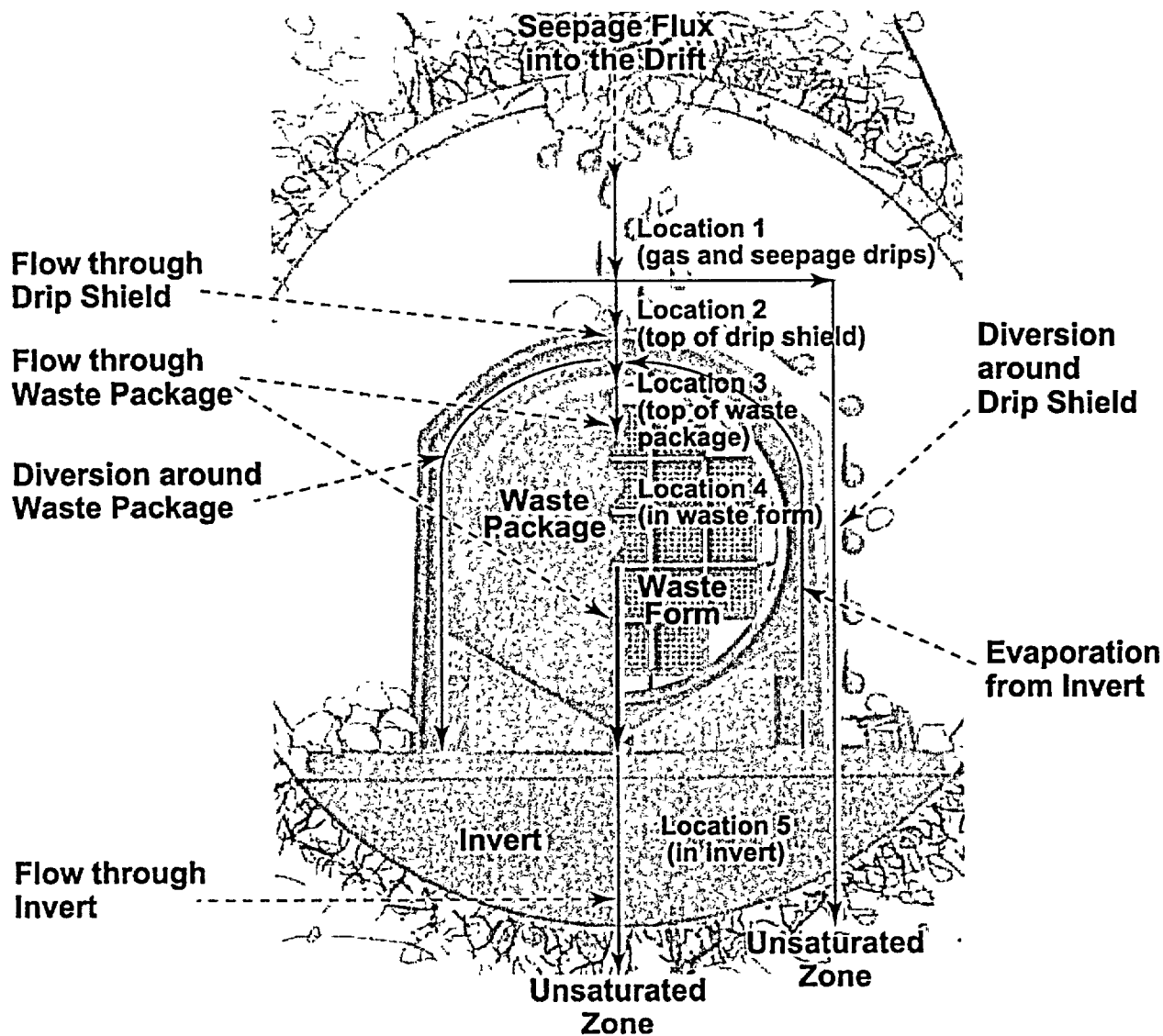


Figure 1. General Engineered Barrier System Design Features, Initial Water Movement, and Rockfall within Drifts Surrounded by the Unsaturated Zone of the Host Rock



NOTE: Not shown is the wicking of water into the invert from the host rock, or any cement-grout interaction flux

Figure 2. Locations of Important Interfaces and Fluxes in the EBS

A generalized representation of EBS design features, initial water movement, and potential rockfall within the emplacement drifts is given in Figure 1. Waste forms are contained in metal waste packages. These packages lie on pallets that rest on a flat invert composed of crushed host rock and metal beams. A titanium alloy drip shield, resting on the invert, covers the waste package. Drip shields are intended to divert entering water, preventing it from contacting the waste packages. Eventually, some drip shields may degrade and develop gaps. If a drip shield is breached, it only partially shields the waste packages from seepage water. Waste packages may be breached by corrosion, which may lead to degradation of the waste forms and release of radionuclides to the invert and the unsaturated zone (UZ) of the host rock.

A sequence of events and processes may occur along the pathways and at the critical locations (Figure 2). However, the events, processes, and sequences that occur at a particular location can differ from those occurring at other locations. For example, some waste packages may be breached, but they may never be contacted by water seepage. For these waste packages, diffusion rather than advection would be the dominant transport mechanism.

When conditions for seepage allow, seepage water may enter the drift by gravity (i.e., by dripping; Figure 2). The composition of this water may have been chemically altered by reactions with ground support materials (e.g., cementitious grout, rock bolts, and other ground support components) and with gases in the host rock. The water may then fall through the air gap above the drip shield where further reactions with in-drift gases can occur. Microbial activity and reactions with EBS materials anywhere in the drift may alter the in-drift gas composition. Interactions with ground support materials and reactions with gases are considered to be part of Location 1 (Figure 2).

After passing through the air gap above the drip shield, the water may contact the surface of the drip shield (Figure 2, Location 2), where it is diverted away from the waste package. Water evaporation, salt precipitation, aqueous solution formation by rewetting and hygroscopic behavior of precipitated salts, and microbial activity may occur on the drip shield. Aqueous solutions can initiate and maintain corrosion, which can breach the drip shield, and microbial activity can accelerate corrosion. Corrosion products on the surface of the drip shield can further alter the water composition. As long as it is intact, the drip shield will divert water fluxes to the invert and UZ.

If the drip shield is breached, seepage water can pass through the breaches and contact the surface of the waste package (Figure 2, Location 3), where it is diverted to the invert until the waste package is breached. Potential evaporation, condensation, and chemical processes at the surface of the waste package are the same as those for the drip shield. Aqueous solutions can initiate corrosion that can breach the waste package, microbial activity can accelerate corrosion, and corrosion products can further alter the water composition. Under appropriate conditions, water can condense under the drip shield, and water reflux can occur between hotter and cooler locations.

If water passes through breaches in the waste package, it will contact the waste forms (Figure 2, Location 4), where radionuclides can be mobilized in water as dissolved or colloidal species. Water may also condense from water vapor on waste forms. Overall, water composition will also be modified by chemical reactions with the waste and other internal waste package components.

Advection and diffusion in flowing water and condensed water films can transport radionuclide-containing species through materials inside the waste package, through breaches in the waste package, and across waste package and pedestal surfaces to the invert (Figure 2, Location 5).

Water can enter the invert (Figure 2, Location 5) from direct seepage, diversion by the drip shield, diversion by the waste package, reflux, flow from the waste package, imbibition or wicking from host rock (not shown in Figure 2), or flow directly from the host rock below the

surface of the invert. Dissolved constituents can also diffuse in water and water films from the waste package to the invert.

All waters entering the invert (Figure 2, Location 5) can mix, yielding a water composition that determines the maximum stable concentrations of dissolved and colloidal radionuclides as determined by solubility and colloid stability models. If dissolved and colloidal radionuclide concentrations exceed solubility and stability limits, the concentrations would be reduced to the limiting values. If the concentrations were below the limits, they would not be adjusted. The resulting radionuclide concentrations are the source term for transport to and through the UZ.

The processes described above occur in a high gamma flux field. Due consideration was given to this aspect of the environment and the conclusions reached in this report are not altered based on the gamma flux present.

3.1.3 Onsager Couplings and Direct Transport Processes in the EBS

Two categories of coupled processes (Onsager couplings and direct transport), that have been discussed in past analyses of the Yucca Mountain environment, are illustrated in Table 1. Onsager couplings are driven indirectly by gradients of thermodynamic state variables (e.g., temperature, pressure, chemical potential, and electrical potential) that affect chemical transport in aqueous solution. Direct transport processes are driven by the same thermodynamic state variables in well-known relations such as Fourier's Law, Darcy's Law, Fick's Laws, and Ohm's Law (Carnahan 1987, p. 2).

Table 1. Onsager Couplings and Direct Transport Process Fluxes Driven by Temperature, Pressure, Chemical Potential, and Electrical Potential Gradients

Flux	Gradient			
	Temperature	Pressure	Chemical Potential	Electrical Potential
Heat Flux	Fourier's Law —heat flow in a temperature gradient	Thermal filtration—heat flow in a pressure gradient	Dufour effect—heat flow in a density gradient	Peltier effect—heat flow in a voltage gradient
Volume Flux	Thermal Osmosis—volume flow in a temperature gradient	Darcy's Law —volume flow in a pressure gradient	Chemical Osmosis—volume flow in a concentration gradient	Electro-osmosis—volume flow in a voltage gradient
Mass Flux	Soret effect—particle flow in a temperature gradient	Reverse Osmosis—mass flow in a pressure gradient	Fick's Law —Mass flow in a concentration gradient	Electrophoresis—mass flow in a voltage gradient
Electrical Flux	Seebeck effect—electrical current in a temperature gradient	Streaming current—electrical current in a pressure gradient	Sedimentation Current—electrical current in a density gradient	Ohm's Law —Current flow in a voltage gradient

NOTE: Onsager couplings and direct transport processes (bold type along diagonal) after Carnahan (1987, p. 2). These Onsager couplings are important only when aqueous, liquid, or solid diffusion dominates over advection.

The direct transport processes produce straightforward transport equations, which have been well known for decades. In contrast, Onsager couplings have generally been examined mathematically or with some laboratory experiments but usually have not been derived for field applications.

3.1.4 The Value of the Simplest Scientific Hypothesis in Isolating Second-order Processes

One fundamental concept used in evaluations of coupled processes in the EBS P&CE models and submodels: the simplest scientific hypothesis is usually accepted unless there are specific facts which preclude the simplest hypothesis from being the correct explanation (Cloud 1970, p. 3-4). The importance of this for examination of coupled processes is that the direct transport processes which are portrayed in bold on the diagonal of Table 1 (Fourier's Law [heat flow in a temperature gradient], Darcy's Law [volume flow in a pressure gradient], and Fick's Law [mass flow in a concentration gradient]) are usually considered in designing physical-chemical process hypotheses on the Yucca Mountain Site Characterization Project (YMP).

If the commonly considered direct transport processes can successfully explain or predict the range of processes for the range of input variables and boundary conditions considered, Onsager couplings (those not in bold type off the diagonal in Table 1) are considered to be second order or lower effects. This means if indirect Onsager couplings (those not on the diagonal in Table 1) are applicable to a given model, they would not be considered to have important effects. Other, more detailed evaluations of coupled processes are done through comparisons of theoretical, laboratory, and field data as described below.

3.1.5 Important Coupled Processes and Locations where Diffusion Dominates

The direct transport processes (bold type in Table 1) are important when diffusion controls transport within the system. When advection becomes a dominant process, these diffusive processes become relatively unimportant. This implies that diffusionally driven Onsager couplings are less significant than by gaseous or aqueous advective transport and that such couplings may be effectively screened out of incorporation into the abstractions of the thermal-hydrological-chemical (THC) type models.

The row for electrical flux and the column for electrical potential gradient in Table 1 may be considered to have a minimal effect on transport in the natural lithostratigraphy and waters at Yucca Mountain, except where voltage leakage or induction from man-made power sources occurs or where corrosion potentials between metals, minerals, and solutions occur. For the cases when a significant gradient does not exist, the three blocks in the column for electrical potential in Table 1 would be considered to have minimal impact as coupled or direct transport processes. The remaining nine positions in Table 1, showing direct transport Laws and Onsager couplings, could be important at various times and locations in the EBS depending on the relative size of the heat, volume, or mass fluxes and on whether there is a significant temperature, pressure, or chemical potential gradient.

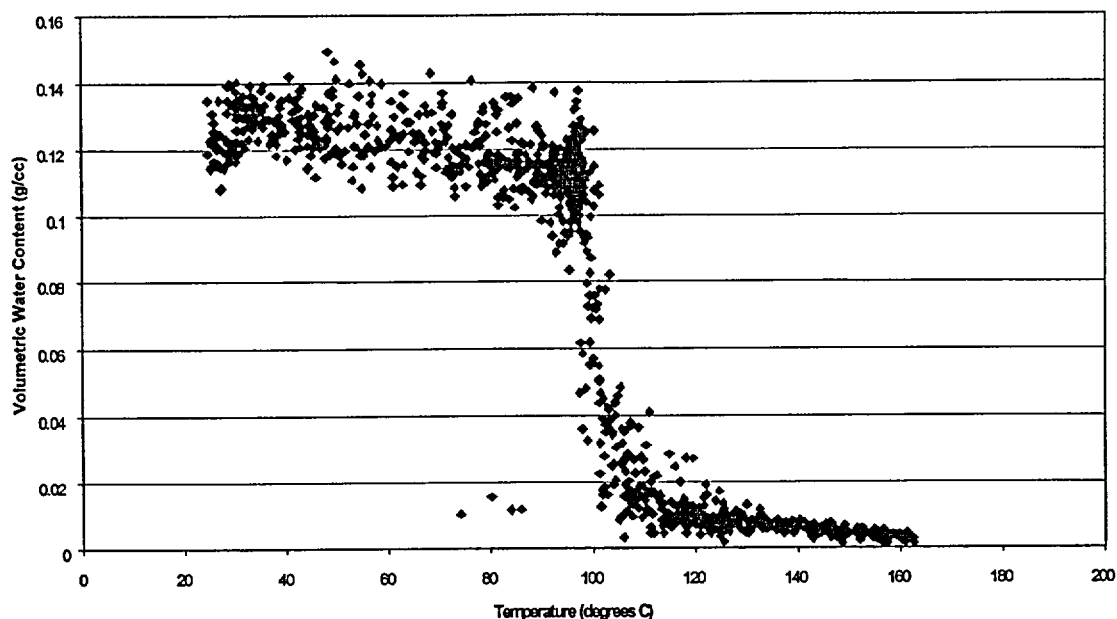
An acceptable criterion for determining a significant temperature, pressure, or chemical potential gradient must be determined with numerical values for a given situation, but generalizations are possible. According to Bird et al. (1960, p. 566), the Dufour energy flux supporting the Dufour effect "is usually of minor importance." Also, "The thermal diffusion term [Soret effect] describes the tendency for species to diffuse under the influence of a temperature gradient; this effect is quite small..." (Bird et al. 1960, p. 565 to 567). In the EBS, areas with very steep temperature gradients during the heating pulse will often have temperatures above the boiling point. Therefore, there will be little or no liquid available for thermal diffusion.

For reactive chemical transport processes in the EBS, there are elements of Onsager-coupled chemical transport and direct effect chemical transport processes (Table 1) that are used in various parts of the EBS models. For example, in the acid neutralizing capacity/pH (ANC/pH) mixing model (which will be fully documented in the next revision of the EBS P&CE model report), water and chemical mass usually are conserved through linear relations (direct transport relations), although there is a mixing factor function based on Fickian diffusion of chemical mass from waste package leakage (BSC 2001a, especially Equation 6-5, p. 6-48). Temperature may alter equilibrium constants and activity coefficients that affect chemical transport indirectly in later implementations. The geochemical databases that support EQ3/6 chemical speciation calculations and the ANC/pH mixing model are currently being upgraded to deal with temperatures up to 300°C, and 100°C, respectively.

Carnahan (1987, p. 9) and Hardin and Chesnut (1997, pp. ES1 to ES16) have made general points for future analysis of coupled processes at Yucca Mountain. Carnahan (1987) concluded that some level of coupling between geochemical and hydrological models is needed for performance assessment; that the development of large, directly coupled hydrogeochemical computer programs is generally undesirable; and that the application of relatively simple coupled models are important aids to understanding.

Figure 3 evaluates the observed *in-situ* relationship between temperature and *in-situ* volumetric water content (from neutron logging) in Borehole EFS-HD-79-TEMP1 (known as Borehole 79) during the drift scale test from February 1998 to May 2000. These data will be used to screen out elevated temperatures (above 133°C) for coupled processes (like the Soret effect) that depend on the geochemical flow of liquid water. These data also will be used to limit the maximum liquid water temperatures needed for high-temperature equilibrium constants in geochemical modeling.

Chemical reactions between high temperature (105 to 180°C) water vapor and minerals, colloids, and metals in the EBS are expected to be common. However, macro-scale geochemical reactions with liquid water that can flow are not expected in the EBS for temperatures above 133°C, based on the field measurements made for the location, elevation, bedrock type, porosities, residual water saturations, and geometry over a large length scale (over 40 m of instrumented borehole) that would exist in the proposed repository (Figure 3). It is likely that at 105 to 133°C (Figure 3), most of the water released from these rocks is water vapor evolved from the thermal dehydration of interstitial waters and waters of mineral hydration (Flint 1998, p. 38) and that little water moves through the EBS environment in the liquid phase at temperatures above 105°C.



DTNS: MO9807DSTSET01.000, MO9810DSTSET02.000, MO9906DSTSET03.000, MO0001SEPDSTPC.000, MO0007SEPDSTPC.001, AND LL000706023101.010

NOTE: This borehole is almost level over an instrumented 40 m section, almost parallel and 9.5 m offset from the center of the drift, and about 3.5 m above the wing heaters that simulate the heat from a waste package. The test was conducted from February 1998 to May 2000.

Figure 3. Experimental Relationship between Borehole Temperature and Volumetric Water Content for Borehole 79 During the Drift Scale Test Over a 2-Year Period During Heating

In summary, if the temperature were greater than 105.5°C, then the volumetric water content would be less than 5 percent (Figure 3). If the temperature were greater than 122.1°C, then volumetric water content would be less than 2 percent. If the temperature were greater than 133.3°C, then the volumetric water content would be less than 1 percent.

Literature and laboratory core sample saturations are in close agreement with observations from the drift scale test (Flint 1998, pp. 32 to 33) drying rock core samples at 60°C and 65 percent relative humidity to simulate that point in saturation where liquid flow stops due to discontinuous columns of water and where vapor flow begins. Flint (1998, pp. 32 to 38) used the standard drying heat of 105°C, which normally is considered to remove most pore waters, but noted that “some, but not all, water was removed from the zeolites, clays, and pore spaces.” The literature surveyed by Flint (1998, p. 38) suggested that most of the water released from 105 to 180°C is from thermal dehydration of zeolites, clays, and interstitial waters.

These generalizations from earlier work suggest that the scatter in temperatures below 5 percent water content (above 105.5°C; Figure 3) is due to the vaporization of water leaving the rock from mineral dehydration. These represent temperatures where water vapor can still play a role in geochemical reactions but where no liquid water flow is expected in or around the EBS environment.

3.1.6 Calculations to Screen Coupled Processes from Consideration

Following the work of Soler (2001), a quantitative spreadsheet calculation has been developed that can be used directly to evaluate the potential effects of coupled transport phenomena on radionuclide transport in the EBS environment. The chemical solute fluxes are computed for advection, chemical diffusion, chemical osmosis, thermal diffusion, thermal osmosis, and hyperfiltration terms using an analytical solution of a one-dimensional transport equation and boundary conditions reported by Ogata and Banks (1961). This approach allows direct, quantitative integration between thermal-hydrological modeling flux results and geochemically coupled process results. It also focuses on the measured rock, thermal, and hydrological properties that are important in any sensitivity analyses of the coupled transport model.

Present work has focused on conversion of Soler's algorithm (Soler 2001, Equations 5 through 24) into a form easily suited to spreadsheet calculation of entered material transport properties. These are summarized below.

The simplest chemical transport processes in the EBS are those that involve nonvolatile dissolved solutes that neither chemically react nor physically adsorb to the inert solids. The three-dimensional advection-dispersion-diffusion relation for contaminant transport or breakthrough for those solutes whose vapor phase is negligible is analyzed by solving the general partial differential equation (PDE) (Fetter 1993, p. 53):

$$\left[\frac{\partial}{\partial x} \left(D_x \cdot \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \cdot \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \cdot \frac{\partial C}{\partial z} \right) \right] - \left[\frac{\partial}{\partial x} (v_x \cdot C) + \frac{\partial}{\partial y} (v_y \cdot C) + \frac{\partial}{\partial z} (v_z \cdot C) \right] = \frac{\partial C}{\partial t} \quad (\text{Eq. 1})$$

where

C = Solute concentration at location x, y, z and time t (mg/l)

D_x = Dispersion/Diffusion Coefficient in the x direction (m^2/sec)

D_y = Dispersion/Diffusion Coefficient in the y direction (m^2/sec)

D_z = Dispersion/Diffusion Coefficient in the z direction (m^2/sec)

v_x = Average Pore-water velocity in the x direction (m/sec)

v_y = Average Pore-water velocity in the y direction (m/sec)

v_z = Average Pore-water velocity in the z direction (m/sec)

t = Time (sec)

x = Horizontal coordinate (m)

y = Horizontal coordinate (m)

z = Vertical coordinate (m).

Note that the dispersion/diffusion coefficients D_x , D_y , and D_z in the x , y , and z directions include both hydrodynamic dispersion, which is associated with mechanical mixing and diffusion (Fetter, 1993, p. 51). Note that the above equation is applied to a nonhomogeneous anisotropic

saturated media. Jury et al. (1993, pp. 221 to 223) extend the application of the general equation to unsaturated media.

The solution to this PDE in the general case involves variations in the three-dimensional solute flux fields. For the invert, the solute flux fields would vary because of the variations in the unsaturated hydraulic conductivity (K_{us}), of the matrix and active fractures of the surrounding tuff, and the matrix of the crushed tuff invert in response to the flow around the drift void space. It is assumed that radionuclides are released at the centerline of the drift, and flow occurs in the vertical direction in which transverse solute flux and transverse dispersion is neglected. If symmetry is invoked for the two-dimensional case, then the three-dimensional PDE presented above reduces to a one-dimensional equation:

$$\left[\frac{\partial}{\partial z} \left(D_z \cdot \frac{\partial C}{\partial z} \right) \right] - \left[\frac{\partial}{\partial z} (v_z \cdot C) \right] = \frac{\partial C}{\partial t} \quad (\text{Eq. 2})$$

where

D_z = Effective Dispersion/Diffusion Coefficient (m^2/sec)

v_z = Average Pore-water Velocity (m/s) in the vertical direction (m/s).

Expanding the expression for advection according to the chain rule, the following PDE for mass transport is obtained (Jury et al. 1991, p. 223):

$$\left[\left(D_z \cdot \frac{\partial^2 C}{\partial z^2} \right) \right] - \left[C \frac{\partial v_z}{\partial z} \right] - \left[v_z \frac{\partial C}{\partial z} \right] = \frac{\partial C}{\partial t} \quad (\text{Eq. 3})$$

If the velocity is assumed constant, then Equation 3 reduces to the standard advection-dispersion-diffusion equation:

$$\left[\left(D_z \cdot \frac{\partial^2 C}{\partial z^2} \right) \right] - \left[v_z \frac{\partial C}{\partial z} \right] = \frac{\partial C}{\partial t} \quad (\text{Eq. 4})$$

Since the centerline of the drift represents a line of symmetry, the horizontal solute flux is zero. Note that while the release of the radionuclides might advect, disperse, or diffuse in the radial direction from the point of release, it is conservative to assume flow in the vertical direction. Assuming that the concentration is equal to one at the top of the invert and the solute flux is constant for steady state flow, then Equation 4 reduces to the one-dimensional advection-dispersion equation, which can be solved using a closed-form analytical solution.

A solution to the above relation is presented by Ogata and Banks (1961, Eq. 13) for non-retarded transport in one dimension with initial concentration C_0 at a continuous rate in which the vapor phase transport is negligible:

$$\frac{C_L}{C_0} = \frac{1}{2} \cdot \left(\operatorname{erfc} \left(\frac{L - v_z \cdot t}{2\sqrt{D \cdot t}} \right) + \exp \left(\frac{V \cdot L}{D} \right) \cdot \operatorname{erfc} \left(\frac{L + v_z \cdot t}{2 \cdot \sqrt{D \cdot t}} \right) \right) \quad (\text{Eq. 5})$$

where

C_L = Solute concentration of the solute at location L and time t (mg/l)

C_0 = Solute concentration of the solute at location z = 0 (mg/l)

D = Dispersion/Diffusion Coefficient (m²/sec) (D_e/θ)

D_e = Effective Dispersion/Diffusion Coefficient (m²/sec)

L = Length in the vertical direction (m)

The solute fluxes (kg/m²/s) associated with advection, chemical diffusion, chemical osmosis, hyperfiltration, thermal diffusion, and thermal osmosis in the vertical direction are given by (Soler 2001, p. 66):

$$\text{Advection } (J_{ADV}) \quad J_{ADV} = -C_L \cdot K \frac{\partial h}{\partial z} \quad (\text{Eq. 6})$$

$$\text{Chemical diffusion } (J_D) \quad J_D = -D_e \cdot \frac{\partial C_L}{\partial z} \quad (\text{Eq. 7})$$

$$\text{Chemical osmosis } (J_{CO}) \quad J_{CO} = C_L \cdot \sigma \cdot K \frac{\partial \Pi_h}{\partial z} \quad (\text{Eq. 8})$$

$$\text{Hyperfiltration } (J_{HYP}) \quad J_{HYP} = C_L \cdot \sigma \cdot K \frac{\partial h}{\partial z} \quad (\text{Eq. 9})$$

$$\text{Thermal diffusion } (J_{TD}) \quad J_{TD} = -D_e \cdot s \cdot C_L \cdot \frac{\partial T}{\partial z} \quad (\text{Eq. 10})$$

$$\text{Thermal osmosis } (J_{TO}) \quad J_{TO} = -C_L \cdot k_T \cdot \frac{\partial T}{\partial z} \quad (\text{Eq. 11})$$

Where

J_{ADV} Advective solute flux (kg/m²/s)

J_D Chemical-diffusive solute flux (kg/m²/s)

J_{CO} Chemical-osmotic solute flux (kg/m²/s)

J_{HYP} Hyperfiltration solute flux (kg/m²/s)

J_{TD}	Thermal-diffusive solute flux (kg/m ² /s)
J_{TO}	Thermal-osmotic solute flux (kg/m ² /s)
K	Hydraulic conductivity (m/s)
h	Hydraulic head (m)
σ	Coefficient of osmotic efficiency (dimensionless)
Π	Osmotic pressure (Pa) Note that the osmotic pressure equals

$$\Pi = -(R \cdot T) / V_w \cdot \ln(a_w)$$

R	Gas constant (J/mol/K)
T	Absolute Temperature (K)
V_w	Molar volume of water (m ³ /mol)
A_w	Activity of water (dimensionless)
Π_h	Osmotic pressure head (m) equal to $\Pi/(\rho \cdot g)$
ρ	Density of fluid (kg/m ³)
g	Gravitational acceleration (m ² /s)
s	Soret coefficient (K ⁻¹)
k_T	Thermo-osmotic permeability (m ² /K/s)

If the hydraulic head (∇h), osmotic pressure ($\nabla \Pi_h$), and temperature gradients (∇T) are assumed to be constant along a one-dimensional section of the EBS invert, and assuming also constant porosity (ϕ), effective diffusion coefficient (De), hydraulic conductivity (K), osmotic efficiency (σ), Soret coefficient (s), and thermo-osmotic permeability (k_T), all solute fluxes can be incorporated into a transport equation of the form in Equation 4. Note that Soler (2001, p. 70) presents analysis for saturated conditions that can be extended to unsaturated by substituting the volumetric moisture content (θ = volumetric moisture content times ϕ) for the porosity:

$$v = \frac{-K \cdot \frac{\partial h}{\partial z} + \sigma \cdot K \cdot \frac{\partial \Pi_h}{\partial z} + \sigma \cdot K \cdot \frac{\partial h}{\partial z} - D_e \cdot s \cdot \frac{\partial T}{\partial z} - k_T \cdot \frac{\partial T}{\partial z}}{\theta} \quad (\text{Eq. 12})$$

Table 2 gives a framework to provide a discussion of the estimation of parameters from several analyses that are available for boundary conditions in the invert at 1900 years. These preliminary data are currently being used for information about the availability of these sorts of parameters to the project. The actual calculations using these or other appropriate data are not

included until a full evaluation of the potential fields in both space and time are conducted and an actual agreement can be made as to which parameters are appropriate.

As a verification of the methodology that the EBS department intends to use in screening out these coupled processes, the calculations that reproduce Soler's graph (2001, Figure 3, p. 74) are included and shown in Figures 4 and 5. Given his inputs, Soler screened out the coupled transport term for thermal diffusion for a proposed Swiss high-level waste repository. However, the importance of this analysis for the YMP is that although the range of Soret coefficients used is from 0 to 0.1 K^{-1} (Figures 4 and 5), which is about an order of magnitude larger than reported Soret coefficients in the literature, the effect of the thermal diffusion term is negligible in comparison to advection and chemical diffusion (i.e., the curve shape is unaffected by the Soret coefficients used).

A future revision of the EBS P&CE model report will focus on obtaining a full set of integrated property measurements from the site-specific THC measurements at Yucca Mountain like those found on Table 2 for the associated flux terms from Equations 6 through 12. A sample of the preliminary calculations with mixed data sets from the YMP and the Swiss project (when site-specific values were not immediately available in the form needed) indicate as shown on figures 4 and 5 that the off-diagonal Onsager coupled processes (Table 1) for the Soret effect are negligible transport processes

Table 2. Preliminary Parameters to Determine the Importance of Coupled Processes in the Invert 1900 Years after Waste Emplacement.

Parameter	Symbol	Value	Units	Source
Intragranular Porosity	ϕ_{matrix}	0.131	(-)	BSC 2001c, Table 4-2
Intergranular Porosity	$\phi_{intergrain}$	0.45	(-)	BSC 2002
Bulk Volumetric Moisture Content	θ_{bulk}	0.061	(-)	BSC 2002
Hydraulic Conductivity	K	6 00E-11	m/sec	BSC 2001c, Table 4-2
Hydraulic Gradient	$\partial h/\partial x$	1.1	m/m	BSC 2001c, Figure 6-76
Coefficient of Osmotic Efficiency	σ	0.00-0.63	(-)	Soler 2001, p. 68; Malusis and Shackelford 2001
Osmotic Gradient	$d\pi/dx$	1-10	m/m	Soler 2001, p. 68
Dispersivity	λ	0.1	m	BSC 2002
Hydrodynamic Dispersion	$\lambda * V$	4.88E-11	m ² /sec	Calculated
Free Water Diffusion Coefficient	D_w	2.30E-09	m ² /sec	BSC 2001d, Eq. 6.4.1-9
Soil Liquid Diffusion	$D_{sl}(\theta, \phi) = D_w / \theta_{bulk}^{1.849}$	1.3 E-11	m ² /sec	BSC 2001d, Eq. 6.4.1-9
Effective Diffusion Coefficient	D_e	6.2 E-11	m ² /sec	BSC 2002
Diffusion Coefficient	$D = D_e / \theta_{bulk}$	4.8 E-10	m ² /sec	Calculated
Soret Coefficient	S_o	0.001-0.1	K ⁻¹	Soler 2001, pp. 69 to 74
Thermal Gradient	$\partial T/\partial x$	0.69	(-)	BSC 2001c, Figure 6-75
Thermo-osmotic Permeability	k_T	1E-14-1E-10	m ² /K/sec	Soler 2001, p. 68

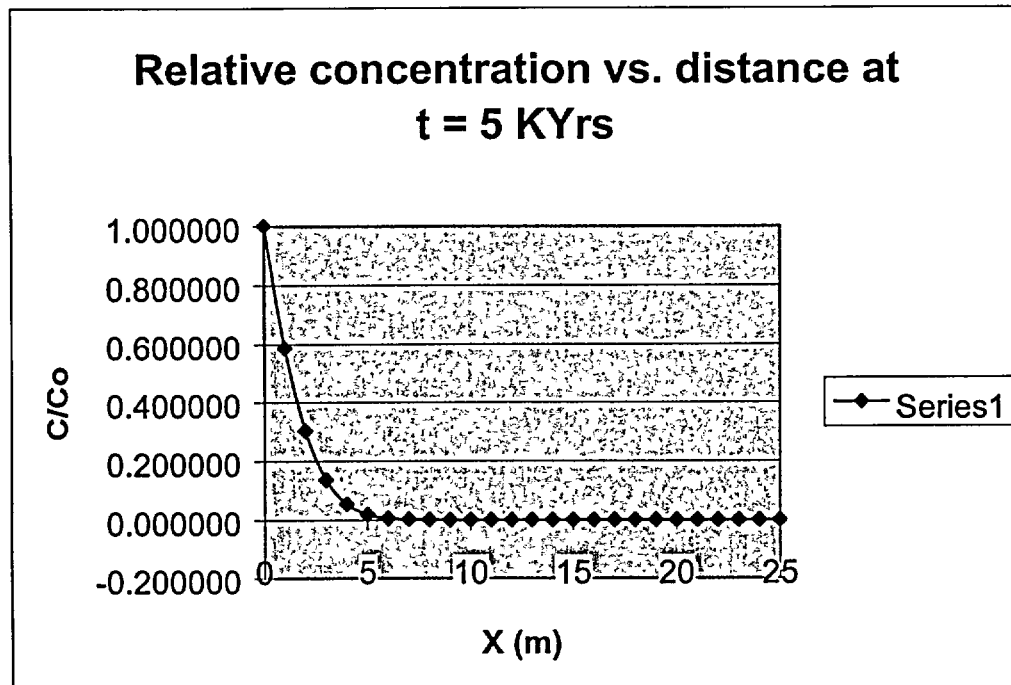
Note: These conditions may not be representative over the entire EBS or the scale of the entire repository.

3.1.7 EBS Coupled Processes in the TSPA for Site Recommendation

In the analyses of the EBS environment, some physical processes have always been coupled to chemical and geochemical processes. For example, every EQ3/6 or PHREEQC geochemical speciation model calculation is coupled indirectly to the temperature gradient at the site through equilibrium constants, which are temperature dependent. In addition, activity coefficients are temperature dependent in speciation calculations.

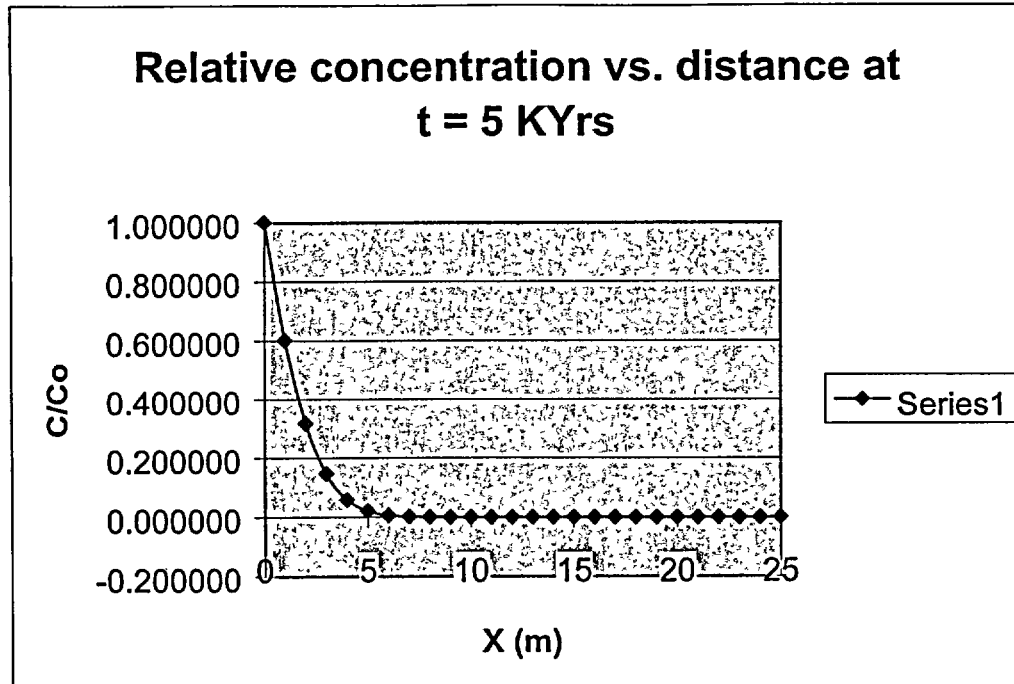
Several essential system attributes of the TSPA for site recommendation directly show the effects of coupled processes. Effects on unsaturated zone flow by flow fields affected by thermal hydrology limited the amount of water contacting the waste package for a given time (CRWMS M&O 2000a, p. 38, Table 4-1). Effects on unsaturated zone transport by sorption distribution

coefficients, varying as a function of isotope and rock type, slowed transport away from the EBS (CRWMS M&O 2000a, p. 45, Table 4-1, Section 6.3.6.1). Drift-scale coupled processes, including thermal hydrology, also limited the amount of water contacting the waste package (CRWMS M&O 2000a, p. 113).



NOTE: Coupled transport terms include advection and chemical diffusion (but with no thermal diffusion), with property values from the Swiss proposed repository for algorithm verification. In this case, the Soret coefficient = 0, corresponds to no thermal diffusion.

Figure 4. Relative Radionuclide Concentration versus Distance in Meters Traveled by a Contaminant Plume Occurring 5000 years after Waste Package Failure



NOTE: Coupled transport terms include advection, chemical diffusion, and thermal diffusion with property values from the Swiss proposed repository for algorithm verification. In this case, the Soret coefficient = 0.1 K^{-1} , corresponds to an upper bound an order of magnitude greater than the range of coefficients found in the literature (10^{-3} to 10^{-2} K^{-1} ; Soler 2001, p. 69). Since there is no change in the contaminant plume shape over an order of magnitude greater than the entire range of Soret coefficients in the literature, this indicates the thermal diffusion process may be screened out for consideration as a significant radionuclide transport process for the given boundary conditions.

Figure 5. Relative Radionuclide Concentration versus Distance in Meters Traveled by Contaminant Plume 5000 years after Waste Package Failure

3.2 ENFE 2.08

3.2.1 Introduction

In KTI agreement EFNE 2.08, the NRC requested that the DOE provide a stronger technical basis for the suppression of individual minerals predicted by equilibrium models. The DOE made the commitment that additional technical bases would be provided for the suppression of individual minerals predicted by equilibrium models. The planned official documentation of this commitment is in a revision to the Engineered Barrier System (EBS): Physical and Chemical Environment (P&CE) Model (CRWMS M&O 2000b). Current project schedules project the finalization of this document in fiscal year 2003.

The primary reaction path equilibrium model that will be used in the next revision to the P&CE model is developed in the In-drift precipitates/salts (IDPS) model (BSC 2001b). Thus, the response below to KTI ENFE 2.08 will discuss the suppression or inclusion of minerals in EBS geochemical modeling and will focus on the mineral suppressions to be documented in the next revision of the IDPS model and the P&CE model.

In order to understand the technical basis for why minerals are included in or excluded from the EBS IDPS and P&CE models, it is important to understand geochemical modeling methodology

in considerable detail. These details allow the modeler to establish the correct framework behind the selection of suppressed minerals. Unfortunately, no literature source or project document currently describes this type of modeling process in enough detail to allow for an extremely abbreviated discussion of the process. Therefore, Figure 6 was developed to show in a simplified way the process steps that are required to suppress or include mineral phases in equilibrium models. The process steps outlined below are to be processed with an understanding of the geochemical boundary conditions at Yucca Mountain. Without that understanding, serious errors could occur in the determination of which mineral assemblage would be relevant.

3.2.2 Geochemical Modeling Methodology

Generally, a reaction path geochemical equilibrium model is constructed using the following steps as outlined in Figure 6. First, a conceptual model is defined where the chemical system and state are defined. This system and state are then tested and investigated to produce results. Then those results are compared with independent experimental, natural analogue, or other modeling data to ensure that the model is representative of the system and state one is trying to analyze.

Decisions about mineral suppression or inclusion require:

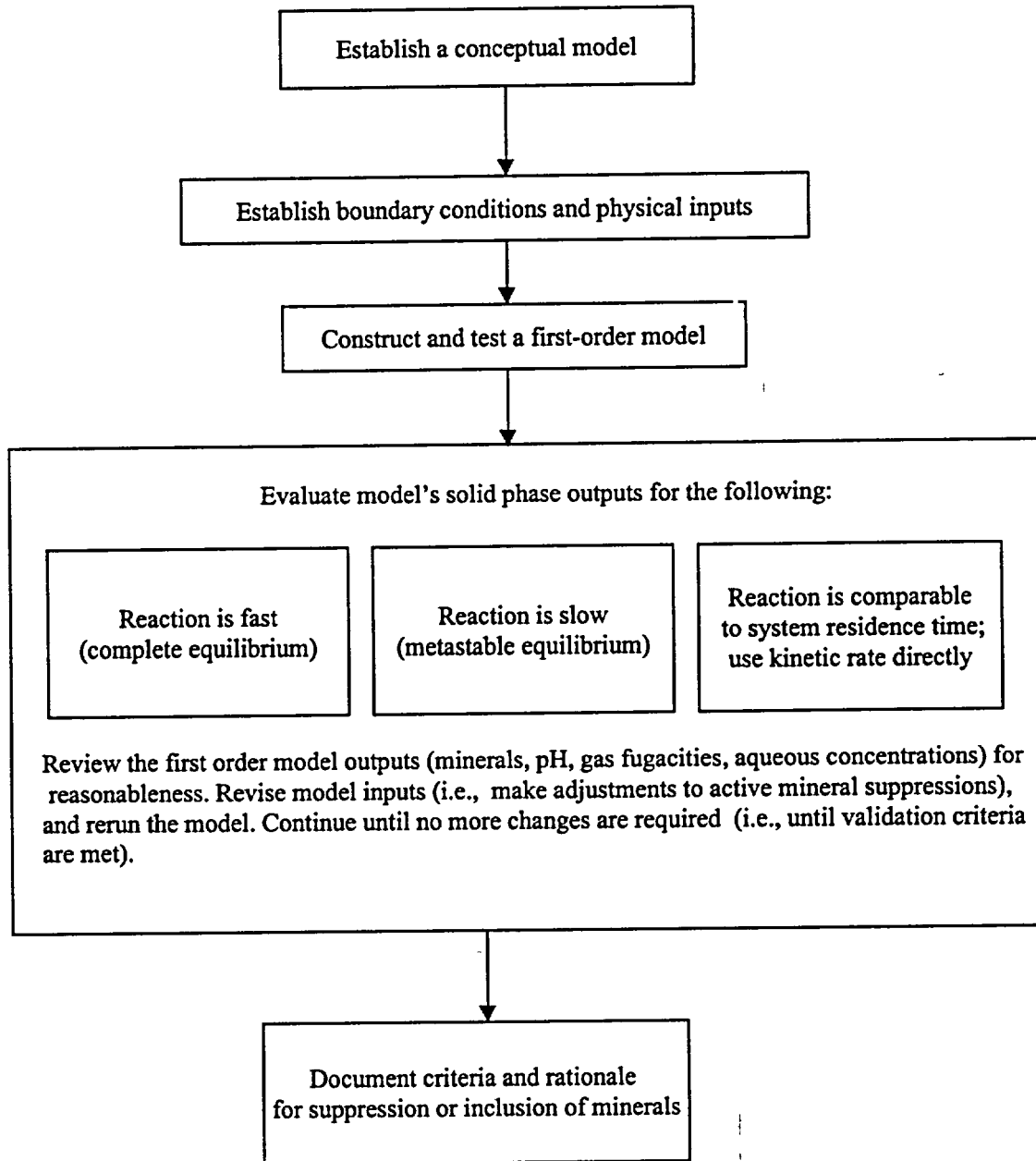
- The modeler to have a reasonable understanding of mineralogy and petrology
- A well researched conceptual model
- An understanding of how to develop a reaction path model using software codes like EQ3/6 (Wolery 1992; Wolery and Daveler 1992), PHREEQC (Parkhurst 1995), or MINTEQA2 (HydroGeoLogic 1999)
- An understanding of how to ensure that the modeler has confidence in the model or has accounted for model uncertainty.

Below is a brief summary of the understanding of kinetics versus equilibrium one must have in order to answer the problems of ensuring the dispositioning of mineral phases are well thought out and have a rational basis. For more detailed discussions on some aspects of modeling methodology, Bethke (1996), Smith and Missen (1991) and Van Zeggeren and Storey (1970) may be consulted.

3.2.3 Equilibrium Versus Kinetics

Bethke (1996, Chapter 2) reports two main types of equilibrium end states that are important to recognize in reaction path modeling: complete equilibrium and metastable equilibrium. In complete equilibrium, the chemical state of the system attains stable equilibrium such that there is no chemical potential to drive any net chemical reaction. Usually when an equilibrium model is first constructed, the first order model (see Figure 6) is allowed to go to complete equilibrium. When the modeler constrains the initial system based on the end equilibrium state by determining things such as the temperature, the dissolved aqueous concentrations, the quantity of given minerals in the system, or the fugacities of any gasses, the calculation result in a fluid that is saturated with respect to the stable equilibrium mineral assemblage for the system.

The Process Required to Give a Valid Technical Basis for Mineral Suppression or Inclusion



NOTE: A First Order Model Is a Model that Accounts for Complete Equilibrium (i.e. No Metastable Equilibrium or Kinetic Controls) with No Active Mineral Suppressions.

Figure 6. A Simplified Roadmap of the Process Required to Give a Valid Technical Basis for Mineral Suppression or Inclusion in Geochemical Equilibrium Modeling

Once a modeler has this first-order model constructed, the modeler evaluates the boundary conditions and the conceptual model to determine if various states of metastable equilibrium should be accounted for. The first-order model is then refined to account for these effects. For example, if the model predicts the complete equilibrium state to include minerals that do not occur in the actual system, then this may imply that a metastable equilibrium situation exists in the actual system.

Metastable equilibrium occurs when one or more chemical reactions proceed toward equilibrium at a rate that is so small on the time scale of interest that the system does not reflect the consequences of reaction with that phase. In this case, the system can be considered to not include the reaction(s) involving that mineral. Such reactions are commonly heterogeneous reactions involving mineral precipitation. That is, the nucleation or growth of the mineral is subject to kinetic barriers that are large enough to allow only negligible progress of the reaction. In such a case, the mineral that should exert an equilibrium compositional constraint is supplanted by another, less stable phase that is not kinetically constrained from forming and growing.

In other words, mineral suppression is used in equilibrium calculations to represent in a simple manner the fact that some solid phases are kinetically inhibited from precipitating or dissolving under equilibrium conditions in certain environments (e.g., quartz precipitation at low temperature). Because of the kinetic constraints, the chemical constituents commonly controlled by the inhibited solid phase are controlled instead by a somewhat less stable phase that reaches its metastable equilibrium rapidly compared to the inhibited phase. Inclusion of the explicit kinetic approaches would handle mineral dissolution or precipitation directly, but for simpler equilibrium calculations this is handled commonly by suppressing the occurrence of that phase in the model to represent the kinetic barrier and to achieve the same result found in real systems. Suppression of minerals, therefore, is a powerful tool in being able to define the end state equilibrium of a modeled system or to use an equilibrium type model to mimic kinetic processes without having to know actual details about the kinetic rates of dissolution or precipitation.

Partial equilibrium and local equilibrium are specific cases or subsets of metastable equilibrium that can have relevance to a given geochemical problem. Partial equilibrium (also known as heterogeneous equilibrium) is defined by Wolery and Daveler (1992) in that some (usually most) reactions are in a state of equilibrium, while others, usually few in number and representing heterogeneous processes such as mineral dissolution or precipitation, are not. As an example, the fluid in a sandstone might be in equilibrium itself but may not be in equilibrium with the mineral grains in the sandstone or with just some of the grains. Local equilibrium, which is sometimes called mosaic equilibrium, can be thought of as a system that is open to groundwater flow. The aqueous phase crosses over or through several different mineral assemblages and the water reacts with each of these and achieves some degree of equilibrium on the local scale with each assemblage, even though each location is at a different state comparatively. All of these various types of equilibrium conditions can be combined into a single model, depending on the conceptual model.

Kinetics can be combined into reaction path modeling because the equilibrium point of a reaction is the point at which dissolution and precipitation rates balance. Bethke indicates that kinetic reactions fall into three groups (1996, Chapter 2).

- Those in which reaction rates are so slow relative to the period of interest that the reaction can be ignored (i.e., accounting for metastable equilibrium). This group corresponds commonly to what mineral suppression is used to represent.
- Those that are fast enough to maintain equilibrium (accounting for complete equilibrium).
- All other reactions that do not fall into the first two groups. These “all other reactions” are the only reactions that require a kinetic description.

3.2.4 EBS Geochemical Equilibrium Modeling

The equilibrium reaction path models used by the P&CE model are designed to predict long-term chemical processes within a potential repository drift. Although short-term occurrences, such as a drop of water falling onto the drip shield, can cause transitory divergence from the conceptualized state of metastable equilibrium, an equilibrium approach is adopted because it provides valuable insight into long-term processes. Though nonequilibrium (or kinetic) modeling might also provide valuable insight, it is not the focus of the subject KTI.

An equilibrium reaction path model relies upon a thermodynamic database that contains the standard state and equation-of-state thermochemical properties of the different chemical species in a system to determine the chemical reaction equilibria as functions of the changing conditions. In addition to the homogeneous reactions that occur within each phase (e.g., water, gas, solid), there are heterogeneous reactions that involve more than one phase, such as mineral precipitation and degassing of volatile constituents from the aqueous phase. Most of the reactions in the equilibrium models employed by the EBS PC&E model are rapid relative to the time frame of the modeling period; therefore, most reactions are allowed to reach equilibrium. However, there are several minerals in the thermodynamic database that are not expected to form under the expected conditions of the repository. These minerals are primarily those that require high pressures or very high temperatures in order to achieve the kinetic rates of formation that would produce a considerable mass within the modeling time frame.

The pressure in the proposed repository is expected to remain near atmospheric, and the temperature at the drift wall is not expected to rise above 200°C. These conditions limit which minerals in the database can be expected realistically to form at a rate that would produce a considerable mass. As discussed above, an equilibrium model ignores the use of kinetic rates; it predicts the most stable mineral phases at equilibrium unless those minerals are suppressed (i.e., ruled out) by the user. When precipitation is suppressed for a mineral, the equilibrium model will not allow the mineral to precipitate resulting in supersaturation of that phase. In this way, the equilibrium model can incorporate simplified kinetic constraints as metastable equilibrium conditions. Current conceptualization of postclosure drift conditions allows for conditions in the proposed repository to be essentially dry. Any seepage entering the drift would be subject to conditions in which the relative humidity or activity of water would fall below one. Therefore, evaporative processes are expected to dominate during the evolution of in-drift seepage.

The new Pitzer thermodynamic database currently has about 220 minerals, but only a small fraction of these have been suppressed in the preliminary modeling runs evaluated to date. It is

unnecessary to identify a priori which of the 220 minerals should be suppressed for these calculations. The limited range of chemical compositions of the waters likely to occur within the drift dictates that a vast majority of the 220 minerals will never achieve a chemical potential favoring precipitation. This point is demonstrated by the preliminary results to date. So far, over 40 different observed and predicted water compositions at Yucca Mountain have been evaporated to dryness using Version 8.0 of EQ3/6 and the new Pitzer database, yet fewer than 40 minerals have become saturated or supersaturated with respect to the aqueous composition. Thus, it would not be an efficient use of time to categorize the remaining 180+ minerals according to their potential for precipitating under drift conditions.

Determining the end equilibrium state in a model is facilitated by having some sort of simple criteria in order to suppress appropriately or include the approximately 40 minerals that have become saturated in the EBS models being developed for TSPA-LA. Five simple criteria have been developed to assist in determining the rationale for suppression or inclusion in the models in order to account for the kinetic or metastable equilibrium arguments stated above. These five criteria are listed below.

Criterion 1—Is the mineral of interest beyond or outside the defined chemical system of the model?

If the mineral lies outside or beyond the defined chemical system of the model, then there is no reason to include the mineral. For example, if one were modeling the reactions between rainwater and a soil derived from the weathering of mafic minerals, one would not expect to form a clay mineral that is known to form from authigenic minerals that are felsic in composition. Likewise, while modeling mineral formation at low temperatures and pressures (near ambient), one could exclude any mineral that was known to form only at high temperatures or pressures.

For individuals trained in mineralogy or petrology, these determinations are readily made. Example reference sources used to make these decisions when combined with expert judgement are Klein and Hurlbut's Manual of Mineralogy (1977), Kerr's Optical Mineralogy (1977) or any reference source that discusses the petrology or mineralogy of a given system or analogue system. One source that could be of use to make some of these determinations for minerals found in the MINTEQA2 database and that are common to EQ3/6 and PHREEQC thermodynamic databases is an online resource for the MINTEQA2 software code (Wadley and Buckley 1997). This information discusses the mineral forms at ambient temperature and pressure and gives comments on their occurrence or formation. The data from this online source has been condensed and summarized in Attachment A. This collection of tabular information (Table A-1) is not only helpful to EBS geochemical modeling as used in Tables 3 and 4 but to other geochemical modelers both on and off the project. The table lists many of the minerals that are in the YMP databases and gives a general idea if the mineral would precipitate under the temperature and pressure boundary conditions that the proposed repository is likely to see.

Criterion 2—Is the mineral of interest likely or unlikely to precipitate because of kinetic controls?

Langmuir (1997) gives a general rule of thumb for determining the need for a kinetic description of mineral dissolution or precipitation. When a reaction is irreversible or its rate is comparable to or slower than the system residence time (i.e., the half-life is greater than or equal to the residence time), a kinetic rate is needed to describe the state of reaction. When this rule of thumb is met and kinetic data are available, a modeler will use them directly. However, often, rate data are not available commonly for the system being modeled, or it is much simpler to invoke a state of metastable equilibrium and use a mineral suppression to simplify the model. Therefore, a modeler will make a mineral suppression that mimics the conceptualized state of metastable or localized equilibrium. As an example, one of the most common mineral suppressions that is used in EBS geochemical modeling is that of considering the kinetic rates of reaction for amorphous silica, quartz, or one of its polymorphs (tridymite and chalcedony). In general, amorphous precipitates will tend to form first, and then a process of mineral recrystallization will take place (Langmuir 1997, p 55). Therefore, the metastable phase that one would generally use in a reaction path model for quartz would be amorphous silica. But if the conceptual model were to account for a longer system residence time or higher temperatures, then the modeler would allow quartz or one of its polymorphs to precipitate. For iron oxides, one would expect either goethite or ferrihydrite to be the metastable phase and hematite to have the longer residence time.

Criterion 3—Is analytical or natural analog information available that warrants the inclusion or exclusion of the mineral?

Often when doing geochemical modeling, the modeler finds information or data in researching the relevant literature used to develop the conceptual model. This information often comes from analytical data or natural analogue information and warrants the suppression or inclusion of minerals that could be dispositioned differently based on an analysis using Criterion 1 and 2. In these instances, the analytical or analogue data will allow for the justification of use. This allows for often-missed minerals that could form due to some unknown kinetic constraint that has not been accounted for directly in the model.

Although care is taken in constructing and attempting to “validate” a model as it is developed, a modeler still has to account for conceptual model or other types of uncertainty. Therefore, some additional criteria would need to be available to include these sorts of suppressions or non-suppressions of mineral phases.

Criterion 4—Do minerals need to be suppressed or included to test overall model uncertainty or sensitivity due to reported uncertainty in the supporting literature, database, or conceptual model?

Criterion 5—Does the suppression or inclusion of minerals that are highly uncertain drive the resulting chemical output to a more or less conservative modeling result?

Certainly, Criterion 4 and 5 are not the normal types of mineral dispositions in models. However, they would be of great use when conducting sensitivity studies or handling modeling uncertainties.

3.2.5 Rationale for Including or Excluding Precipitating Minerals

As a relevant natural analogue to which the IDPS and P&CE conceptual models can be compared for appropriate mineral assemblages, are evaporative minerals that form in saline lakes and playa deposits as documented in sources such as Eugster and Hardie (1978) or Papke (1976). The minerals from these types of evaporitic environments should reflect the mineral assemblages that could form in a low-temperature, low-pressure, in-drift environment where the activity of water is below one and the solution compositions are comparable. Table A-1 (Attachment A) is used in conjunction with the model boundary conditions in a low-temperature, low-pressure, in-drift environment to strengthen the rationale listed in the tables below.

In addition to the mineral suppression or inclusion rationale listed in the tables below, which definitely adds to the overall model validation, each EBS model is independently validated against natural analogue data, or experimental results to ensure that the model is an appropriate representation. These confidence-building activities occur both during and after model development activities are finalized.

Table 3 provides a listing of the minerals that have been suppressed in modeling efforts that are being conducted to construct the EBS IDPS and P&CE models that will serve as input into the TSPA-LA. Table 4 provides a listing of the minerals that have been allowed to precipitate in models to date that are being conducted to construct the EBS IDPS and P&CE models, which will serve as input into the TSPA-LA.

Table 3. A Listing of MineralSuppressions that Will Be Included in EBS Geochemistry Modeling Documentation for TSPA-LA

Mineral	Formula	Criteria Selected	Rationale	References
Cristobalite (alpha)	SiO ₂	Criterion 2	Cristobalite forms at temperatures greater than 1470°C. At standard temperatures and pressures cristobalite will slowly convert to quartz.	Krauskopf 1979, Figure 14-1; Table A-1
Dolomite	CaMg(CO ₃) ₂	Criterion 2	Although dolomite is a common mineral in evaporite deposits from springs derived from carbonate and tuffaceous waters in southern Nevada at Yucca Mountain, its growth mechanism is slow when compared to the precipitation calcite, opal and Mg-bearing minerals such as sepiolite.	Vaniman et al. 1992; Table A-1
Glaserite	NaK ₃ (SO ₄) ₂	Criterion 4	Although glaserite is a mineral that is expected to form in evaporitic type deposits, the thermodynamic data currently being considered for inclusion in the Pitzer database are questionable.	This mineral would be suppressed, subject to sensitivity analysis.
Magnesite	MgCO ₃	Criterion 4	Magnesite is commonly associated with metamorphic mineral assemblages such as serpentine. There are instances where magnesite is associated with salt deposits, yet it is uncertain that it can form under standard temperatures and pressures as magnesite could be associated with the diagenesis of buried salt deposits.	Kerr 1977; Eugster and Hardie 1978, This mineral would be suppressed, subject to sensitivity analysis.
Maximum Microcline	KAlSi ₃ O ₈	Criterion 1	Microcline is generally associated with the formation of granite, syenite and gneiss. Although it is often found as a common mineral in sandstone or arkose, the occurrence in these instances is detrital and not authigenic.	Kerr 1977, p. 306; Table A-1
Quartz	SiO ₂	Criterion 2	Literature evidence suggests that amorphous silica is at metastable equilibrium with respect to quartz at low temperatures and pressures. This is also evidenced by the precipitation of opal-CT (an amorphous silica phase) as opposed to quartz in evaporated carbonate and tuffaceous waters of southern Nevada.	Langmuir 1997; Vaniman et al., 1992; Table A-1
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	Criterion 1	Talc is characteristically associated with low-grade metamorphic rock and hydrothermal alteration of ultrabasic rocks.	Kerr 1977; Table A-1
Ca-saponite Mg-saponite Na-saponite H-saponite K-saponite	Ca ₀₋₁₆₅ Mg ₃ Al ₀₋₃₃ Si ₃₋₆₇ O ₁₀ (OH) ₂ Mg ₃₋₁₆₅ Al ₀₋₃₃ Si ₃₋₆₇ O ₁₀ (OH) ₂ Na ₀₋₃₃ Mg ₃ Al ₀₋₃₃ Si ₃₋₆₇ O ₁₀ (OH) ₂ H ₀₋₃₃ Mg ₃ Al ₀₋₃₃ Si ₃₋₆₇ O ₁₀ (OH) ₂ K ₀₋₃₃ Mg ₃ Al ₀₋₃₃ Si ₃₋₆₇ O ₁₀ (OH) ₂	Criterion 1	Saponite is a montmorillonite or smectite clay. Smectite clays are commonly associated with fracture linings at Yucca Mountain. However, saponitic clays are associated with the weathering of basalt and not rhyolitic tuffs. Saponite also does not generally form independently from its associated parent material as it does not precipitate independently in soil environments.	Krauskopf 1979; Carlos et al 1995; Deer et al 1966; Borchardt 1989

Table 4. A Listing of Minerals Allowed to Precipitate that will be included in EBS Geochemistry Modeling Documentation for TSPA-LA

Mineral	Formula	Criteria Selected	Rationale	References
Calcite	CaCO_3	Criterion 3	Calcite is a common evaporite mineral formed from evaporated waters of southern Nevada.	Vaniman et al. 1992
$\text{SiO}_2(\text{am})$	SiO_2	Criterion 2	Literature evidence suggests that amorphous silica is at metastable equilibrium with respect to quartz at low temperatures and pressures. This is also evidenced by precipitation of opal-CT as opposed to quartz in evaporated carbonate and tuffaceous waters of southern Nevada.	Langmuir 1997; Vaniman et al. 1992
Fluorite	CaF_2	Criterion 3	Fluorite is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1; Table A-1
Sepiolite	$\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	Criterion 3	Although Table A-1 indicates that sepiolite should not form at ambient temperatures and pressures, precipitation of sepiolite is common in conjunction with calcite precipitation in calcrete deposits. Sepiolite is a common fracture-lining mineral above the basil vitrophyre of the Topopah Spring Member at Yucca Mountain. Sepiolite is also known to commonly form on evaporation of either carbonate-source or tuff-source waters in southern Nevada.	Hay and Wiggins 1980; Carlos et al. 1995; Vaniman et al. 1992
Celadonite	$\text{KMgAlSi}_4\text{O}_{10}(\text{OH})_2$	Criterion 3	Although its occurrence is generally associated with hydrothermally altered mafic volcanic rocks and with illite-chlorite minerals, celadonite is also found as an authigenic silicate mineral in saline, alkaline, nonmarine environments such as playa deposits.	Li et al. 1997; Hay et al. 1966
Nahcolite	NaHCO_3	Criterion 3	Nahcolite is a saline mineral associated with $\text{Na-CO}_3\text{-Cl}$ brines.	Eugster and Hardie 1978, Table 3;
Thenardite	Na_2SO_4	Criterion 3	Thenardite is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1
Halite	NaCl	Criterion 3	Halite is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1; Kerr 1979, page 221; Table A-1
Huntite	$\text{CaMg}_3(\text{CO}_3)_4$	Criterion 3	Huntite is a Mg carbonate mineral associated with cave and evaporite deposits as well as with meteoric (low-temperature) dissolution, and reprecipitation of calcite, dolomite or magnite. Huntite will precipitate instead of calcite when Mg^{2+} is concentrated in solutions with respect to Ca^{2+} due to evaporative processes.	Faust 1953; Walling et al. 1995, page 360

Table 4. A Listing of Minerals Allowed to Precipitate that will be included in EBS Geochemistry Modeling Documentation for TSPA-LA (Continued)

Mineral	Formula	Criteria Selected	Rationale	References
Sellaite	MgF ₂	Criterion 3	Sellaite is the Mg analogue to fluorite that forms in evaporite deposits.	Palache et al. 1951, page 37 to 39
Gypsum	CaSO ₄ ·2H ₂ O	Criterion 3	Gypsum is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1; Kerr 1979, page 221; Table A-1
Glauberite	Na ₂ Ca(SO ₄) ₂	Criterion 3	Glauberite is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1
Niter	KNO ₃	Criterion 3	Niter is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1
Sylvite	KCl	Criterion 3	Sylvite is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1; Kerr 1979, page 221
Arcanite	K ₂ SO ₄	Criterion 3	Arcanite is a very soluble mineral belonging to the Mascagnite group and can be precipitated in the laboratory from the slow evaporation of water solutions. This mineral is related to thenardite and should have similar properties.	Palache et al. 1951, page 398 to 400
Soda Niter	NaNO ₃	Criterion 3	Soda Niter is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1
Carnallite	KMgCl ₃ ·6H ₂ O	Criterion 3	Carnallite is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1; Kerr 1979, page 221
Pentasalt (Gorgeyite)	K ₂ Ca ₅ (SO ₄) ₆ ·H ₂ O	Criterion 3	Gorgeyite occurs in association with glauberite, halite, and polyhalite in salt deposits.	Fleischer 1954
Syngenite	K ₂ Ca(SO ₄) ₂ ·H ₂ O	Criterion 3	Syngenite is associated with salt deposits (especially halite) and is known to be precipitated in cavities created by volcanic action. It precipitates at room temperatures from solutions that contain K ₂ SO ₄ .	Palache et al. 1951, page 442 to 444
Anhydrite	CaSO ₄	Criterion 3	Anhydrite is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1; Kerr 1979, page 221
Natrite	Na ₂ CO ₃	Criterion 3	Natrite is a highly soluble carbonate mineral associated with shortite, pirssonite, and gaylussite. These three minerals are also associated with the precipitation of trona, calcite and montmorillonite and are found in clay beds that have deposited in borax lakes.	Fleischer and Pabst 1983 Palache et al. 1951
Trona	Na ₃ H(CO ₃) ₂ ·2H ₂ O	Criterion 3	Trona is associated with evaporite deposits in Nevada playas.	Papke 1976, Table 1

Table 4. A Listing of Minerals Allowed to Precipitate that will be included in EBS Geochemistry Modeling Documentation for TSPA-LA (Continued)

Mineral	Formula	Criteria Selected	Rationale	References
Burkeite	$\text{Na}_6\text{CO}_3(\text{SO}_4)_2$	Criterion 3	Burkeite is a saline mineral associated with Na-CO ₃ -SO ₄ -Cl brines.	Eugster and Hardie 1978, Table 3
Stellerite	$\text{Ca}_2\text{Al}_4\text{Si}_{14}\text{O}_{36} \cdot 14\text{H}_2\text{O}$	Criterion 3	Stellerite is a zeolite mineral commonly associated with fracture linings at Yucca Mountain.	Carlos et al. 1995
Phillipsite	$\text{K}_{0.7}\text{Na}_{0.7}\text{Ca}_{1.1}\text{Al}_{3.6}\text{Si}_{12.4}\text{O}_{32} \cdot 12.6\text{H}_2\text{O}$	Criterion 3	Phillipsite is a zeolite mineral commonly associated with evaporite deposits.	Hay 1966
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	Criterion 3	Kieserite is an evaporite mineral commonly found in salt deposits. Often it is associated with halite or carnallite.	Palache et al. 1951, page 477 to 479

3.3 SUMMARY OF NEW INFORMATION PROVIDED

3.3.1 ENFE 2.07

Two categories of coupled processes (Onsager couplings and direct transport), that have been discussed in past analyses of the Yucca Mountain environment are illustrated in Table 1. One fundamental concept has been omitted in past evaluations of coupled processes in the EBS P&CE models and submodels: The simplest scientific hypothesis is usually accepted unless there are specific facts which preclude the simplest hypothesis from being the correct explanation (Cloud 1970, p. 3 to 4). The importance of this for examination of coupled processes is that the direct transport processes that are portrayed in bold on the diagonal of Table 1 (Fourier's Law [heat flow in a temperature gradient], Darcy's Law [volume flow in a pressure gradient], and Fick's Law [mass flow in a concentration gradient]) are usually considered in designing physical-chemical process hypotheses on the YMP. If the commonly considered direct transport processes can successfully model the range of processes for the range of input variables and boundary conditions considered, Onsager couplings that are off the diagonal in Table 1 are considered to be second order or lower effects. The Onsager couplings and the direct-transport processes (Table 1) are important when diffusion controls transport within the system. When advection becomes a dominant process, these Onsager couplings may be considered minimized because the processes listed in Table 1 become relatively unimportant. The electrical flux row and electrical potential gradient column (Table 1) may be considered to have a minimal effect in the natural lithostratigraphy and waters at Yucca Mountain, except where voltage leakage or induction from man-made power sources occurs or where corrosion potentials between metals, minerals, and solutions occur.

Figure 3 evaluates the observed *in-situ* relationship between temperature and *in-situ* volumetric water content (from neutron logging) in Borehole EFS-HD-79-TEMP1 (known as Borehole 79) during the drift scale test from February 1998 to May 2000. These data will be used to screen out elevated temperatures (above 133°C) for Onsager couplings (like the Soret effect) that depend on the geochemical flow of macroscale liquid water.

Recently, a quantitative spreadsheet model has been developed that can be directly used to evaluate the potential effects of coupled transport phenomena on radionuclide transport in the YMP EBS environment. The chemical solute fluxes are computed for advection, chemical diffusion, chemical osmosis, thermal diffusion, thermal osmosis, and hyperfiltration terms using an analytical solution of a one-dimensional transport equation and boundary conditions. This approach allows direct, quantitative integration between thermal-hydrological modeling flux results and geochemically coupled process results.

Future revision of the PC&E AMR will focus on using integrated property measurements like those shown in Table 2 for the associated flux terms from Soler (2001), as shown in Equations 6 through 12 of this report for coupled processes from the site-specific THC measurements at Yucca Mountain. Preliminary calculations with mixed data sets from the YMP and the Swiss project (when site-specific values were not immediately available in the form needed) indicate that all of the off-diagonal Onsager couplings (Table 1) are negligible transport processes, except perhaps thermal osmosis.

Based on the information given in this report, a stronger technical basis has been given for the screening out of all off-diagonal Onsager couplings with the possible exception of thermal osmosis in EBS geochemical modeling. This information will be included in EBS modeling documentation that is being prepared for license application. Therefore, this agreement can be closed upon review and acceptance by the NRC.

3.3.2 ENFE 2.08

This report presents a discussion of the appropriate process that governs the selection and suppression of mineral phases in geochemical models (Figure 6). This process has been augmented by defining criteria that assist the modeler in developing the appropriate rationale to adequately screen in or out mineral phases that would normally be predicted based strictly on equilibrium calculations. These criteria (Section 3.2.4) allow equilibrium models to account for metastable equilibrium conditions that are a result of kinetic processes. The result of using the process listed above during the construction of EBS geochemical models for TSPA-LA resulted in Tables 3 and 4 of this report. These tables, along with the ongoing modeling work (including comparing these results to the conceptual models and model validation test cases that are too extensive to include here but will be documented in the appropriate EBS model reports) demonstrate that the EBS geochemical models are appropriate and adequate, these suppressions and precipitates are reasonable, and they support a valid model.

This report presents the technical basis for the suppression of 12 mineral phases and rationale based on literature sources for the inclusion of 26 minerals in the model output to date in calculations using Version 8.0 of EQ3/6 and the new Pitzer database. These technical bases will be finalized and incorporated into the appropriate model reports. Should additional suppressions or inclusions be necessary in future model calculations, the technical basis for these additional minerals will be documented with the results.

Based on the information given above, a stronger technical basis has been given for the suppression of minerals in EBS geochemical modeling. This information will be included in

EBS modeling documentation that is being prepared for license application. Therefore, this agreement can be closed upon review and acceptance by the NRC.

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4.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

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4.3 SOURCE DATA, LISTED BY DATA TRACKING NUMBER

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MO0007SEPDSTPC.001. Drift Scale Test (DST) Temperature, Power, Current, and Voltage Data for November 1, 1999 through May 31, 2000. Submittal date: 07/13/2000.

MO9807DSTSET01.000. Drift Scale Test (DST) Temperature, Power, Current, Voltage Data for November 7, 1997 through May 31, 1998. Submittal date: 07/09/1998.

MO9810DSTSET02.000. Drift Scale Test (DST) Temperature, Power, Current, Voltage Data for June 1 through August 31, 1998. Submittal date: 10/09/1998.

MO9906DSTSET03.000. Drift Scale Test (DST) Temperature, Power, Current, and Voltage Data for September 1, 1998 through May 31, 1999. Submittal date: 06/08/1999.

ATTACHMENT A

Table A-1 can be used as a first order approximation for whether a mineral can precipitate under ambient temperatures and pressures. Minor changes have been made to some mineral names to match those in the current YMP EQ3/6 databases. Minerals marked with an asterisk (*) are not included in YMP databases.

Table A-1. A Modified Listing of Minerals from MINTEQA2 Online Handbook (Wadley and Buckley 1997).

Mineral	Chemical Formula	Precipitates from 0-100 °C and at 1 ATM	Comments on Occurrence or Formation	Refs
Alum-K	$KAl(SO_4)_2 \cdot 12H_2O$	yes	When hot solutions of equimolecular quantities of aluminium sulphate + K-sulphate are mixed, and the solution cooled, octahedral crystals of a double sulphate of aluminium and potassium separate	2, 5
Alunite	$KAl_3(OH)_6(SO_4)_2$	no	Small, imperfect, rare crystals, found in altered or mineralised organic rocks. Crystallised by heating a solution of alum and aluminium sulphate in a sealed tube at 230 °C.	7
Anhydrite	$CaSO_4$	yes	Ppt under conditions of very high supersaturation (high Ca^{2+}/SO_4^{2-}). It forms at temperatures > 40 °C	1, 8
Albite_low	$NaAlSi_3O_8$	yes	Occurs in igneous, sedimentary and metamorphic rocks. Can be formed by heating gelatinous silica, alumina and caustic soda in a sealed tube.	3, 6
Analbite*	$NaAlSi_3O_8$	no	It is disordered albite.	6
Akermanite	$Ca_2MgSi_2O_7$	no	It melts congruently at 1454 and forms a solid solution series with a minimum melting temperature of 1385. Crystallization proceeds from akermanite-rich compositions.	4
Analcime	$NaAlSi_2O_6 \cdot H_2O$	no	It may occur as a primary mineral in some alkaline basic igneous rocks. It occurs as a late-stage hydrothermal mineral, crystallising in vesicles and occurs with zeolites, thomsonites and stillbite.	5
Annite	$KFe_3Al_3Si_3O_{10}(OH)_2$	no	Part of the biotite series. It forms from chlorite in metamorphosed pelitic rocks. It is the primary mineral in acid intermediate plutonic igneous rocks and some basic plutonic rocks.	1
Barite	$BaSO_4$	yes	Frequently found associated with fluorite, calcite, dolomite and quartz. Produced by slow inter-diffusion of dilute solutions of barium chloride and sulphates.	7
Bianchite*	$(Zn,Fe)SO_4 \cdot 6H_2O$	no		5

Table A-1. A Modified Listing of Minerals from MINTEQA2 Online Handbook (Wadley and Buckley 1997) (Continued)

Mineral	Chemical Formula	Precipitates from 0-100 °C and at 1 ATM	Comments on Occurrence or Formation	Refs
Boehmite	AlO(OH)	no	Widely distributed in bauxite. Produced as an intermediate product in the dehydration of gibbsite and by heating precipitated hydrous aluminium oxide or gibbsite under pressure.	7
Brucite	Mg(OH) ₂	yes	Found associated with minerals such as calcite, aragonite, hydromagnesite and artinite. Precipitates with alkalis from solutions of magnesium salts or by hydration of magnesium oxide and reaction of water with magnesium amalgams.	5, 7, 8
Chalcedony	SiO ₂	no	Chalcedony includes a number of substances, eg. Carnelian, sard, prase, bloodstone, agate, flint, jasper.	5
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	no	It is a fibrous serpentine. It is an important variety of commercial asbestos.	5
Enstatite	MgSiO ₃	no	It is part of the pyroxene group and is found in some meteorites.	6
Cristobalite	SiO ₂	no	2 varieties viz. alpha and beta. These are SiO ₂ polymorphs and alpha cristobalite - can exist at atmospheric temperatures up to 200-275 °C. Beta variety exists above 200-275 °C, stable from 1470 °C to its melting point 1713 °C.	4
Corundum	Al ₂ O ₃	yes	How: Prepared in a crystalline condition by strongly heating a mixture of aluminium fluoride and boric acid	2, 6
Diopside	CaMgSi ₂ O ₆	no	Diopside occurs in many metamorphic rocks especially metamorphosed dolomitic limestones and calcareous sedimentary rocks.	5
Dolomite	CaMg(CO ₃) ₂	yes	Precipitated from a solution of MgCl ₂ , CaCl ₂ and urea at highly elevated pressure (higher than 2/3 atm.) at 228 °C.	
Diaspore	α-AlO(OH)	no	It results from the alteration of corundum and emery. It is a basic constituent of bauxite deposits.	5
Epsomite	MgSO ₄ ·7H ₂ O	yes	MgSO ₄ occurs as kieserite, MgSO ₄ ·H ₂ O. When it is digested with water and the solution, purified by re-crystallisation, colourless, rhombic, prisms separate from the cold solution.	2, 6
FCO ₃ apatite*	[Ca ₉₋₄₉₆ Na ₀₋₃₆ Mg ₀₋₁₄₄ (PO ₄) ₄₈ (CO ₃) ₁₋₂ F ₂₋₄₈]	no		

Table A-1. A Modified Listing of Minerals from MINTEQA2 Online Handbook (Wadley and Buckley 1997) (Continued)

Mineral	Chemical Formula	Precipitates from 0-100 °C and at 1 ATM	Comments on Occurrence or Formation	Refs
Fluorite	CaF_2	yes	Most fluorite is 99 % CaF_2 , with small amounts of Si, Al and Mg due to impurities and inclusions. It can be prepared by the evaporation of a solution of CaF_2 in HCl.	4
Forsterite	Mg_2SiO_4	no	It is part of the olivine group. Occurs in crystalline limestones or ultramafic igneous rocks.	5
Gehlenite	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	no	It occurs in basic lava flows that are silica undersaturated.	5
Gibbsite	$\text{Al}(\text{OH})_3$	yes	It is obtained as a colloidal precipitate when ammonia or an alkaline carbonate is added to a solution of an aluminium salt	2, 5
Goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	yes	By acting upon zinc or zinc oxide with dilute sulphuric acid. The concentrated solution deposits transparent crystals of the composition $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.	
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	yes	Prepared by mixing solutions of sulphates with solutions of calcium salts. Some forms by hydration of anhydrite.	2, 5
Halite	NaCl	yes	Formed by evaporation of a highly saturated saline solution.	6
Halloysite*	$\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8 \cdot 8\text{H}_2\text{O}$	no	Similar to kaolinite, but contains interlayered water molecules.	5
Hematite	Fe_2O_3	yes	Prepared by decomposing ferric chloride by steam at high temperature.	3
Hercynite*	FeAl_2O_4	no	It is a iron aluminium oxide of the spinel group.	5
Huntite	$\text{Ca Mg}_3(\text{CO}_3)_4$	no	It occurs as an alteration of dolomite or magnesite-bearing rocks.	4
Hydroxylapatite	$\text{Ca}_5(\text{OH})(\text{PO}_4)_3$	yes	Prepared by precipitation from solutions of calcium salts with the addition of ammoniacal phosphate solutions.	4
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	no	It forms on alteration of feldspars in granites. The alteration can be caused by weathering or by pneumatolytic action of gases on feldspars.	5
Larnite	Ca_2SiO_4	no	It occurs at dolerite - limestone contacts.	5
Lime	CaO	yes	Obtained by igniting calcium carbonate or calcium oxalate at about 800 .	2, 5
Leonhardite*	$\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 3\text{H}_2\text{O}$	no	Forms when laumontite (hydrated calcium aluminosilicate) loses its water.	4

Table A-1. A Modified Listing of Minerals from MINTEQA2 Online Handbook (Wadley and Buckley 1997) (Continued)

Mineral	Chemical Formula	Precipitates from 0-100 °C and at 1 ATM	Comments on Occurrence or Formation	Refs
Leucite*	KAlSi_2O_6	no	Occurs in K-rich basic extrusive lavas that may be silica deficient.	5
Laumonite*	$\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}$	no	Occurs in cavities in igneous rocks, from basalts to granites. It originates from mild metamorphic alteration of volcanic glass and feldspars.	4
Merwinite	$\text{MgCa}_3(\text{SiO}_4)_2$	no	Occurs at gabbro - limestone contacts.	5
Muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	no	Common in the mica group. Found in regionally metamorphosed sediments. It can crystallise from a liquid of granite composition at pressures > 1500 atmospheres.	6
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	no	Mirabilite or glauber salt occurs in the residues of alkali lakes.	4
Manganosic oxide (MnSO_4)	MnSO_4	yes	Manganosic oxide reacts with acid with the formation of a soluble manganous salt and insoluble hydrated manganese dioxide.	2
Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	no	Results from the decomposition of pyrite in the zone of oxidation.	4
Manganous chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$)	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	yes	Manganous chloride is prepared by dissolving the oxide or carbonate in hydrochloric acid and evaporating the solution, the heating being continued long enough to drive off all the free chlorine.	7
Monticellite	CaMgSiO_4	no	It occurs in metamorphic and metasomatized siliceous dolomitic limestones at contacts with both basic and acid igneous rocks.	
Maximum_ Microcline	KAlSi_3O_8	no	It is a constituent of alkali acid igneous rocks. It is abundant in granites and syenites and are cooled slowly at depth.	4
Nepheline	$\text{NaAlSi}_3\text{O}_8$	no	Nepheline is a characteristic primary crystallising mineral of alkaline igneous rocks.	6
Natron	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	no	It is found in solution in soda-lakes.	1
Periclase	MgO	yes	It is made by heating MgCO_3 or the hydroxide obtained from sea- H_2O .	1
Pyrophyllite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})$	no	It occurs as a secondary product from hydrothermal alteration of feldspar. It occurs as foliated masses in crystalline schists.	5

Table A-1. A Modified Listing of Minerals from MINTEQA2 Online Handbook (Wadley and Buckley 1997) (Continued)

Mineral	Chemical Formula	Precipitates from 0-100 °C and at 1 ATM	Comments on Occurrence or Formation	Refs
Phlogopite	$KAlMg_3Si_3O_{10}(OH)_2$	no	It occurs in metamorphosed limestones and ultrabasic rocks. It is a product of regional metamorphism of impure magnesium limestones. It is derived from the reaction between dolomite and potassium feldspar.	5
Portlandite	$Ca(OH)_2$	yes	Formed on addition of water to CaO. Another way is to heat aqueous solutions of calcium salts with alkalis.	2
Pyrochroite*	$Mn(OH)_2$	no	It is a hydrothermal mineral.	
Quartz	SiO_2	no	Essential constituent of acid igneous plutonic rocks eg granites. Also present in extrusive and hypabyssal rocks. Also found in conglomerates, arenites, siltstones and mudstones	1
Rhodochrosite	$MnCO_3$	yes	Made by adding sodium carbonate solution to a solution of manganous salt.	
Siderite	$FeCO_3$	yes	By heating $(NH_4)_2 CO_3$ with $FeCl_2$	4
Sepiolite	$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$	no	Found in beds of irregular masses in alluvial deposits derived from serpentine masses.	1, 6
Sanidine_high	$KAlSi_3O_8$	no	High temperature K-Feldspar which has been quickly cooled as in extrusive igneous rocks has a tabular form and is called sanidine.	5
Spinel	$MgAl_2O_4$	yes	It is a common high temperature mineral in metamorphic rocks and aluminium xenoliths. Occurs in contact metamorphosed limestones. It may be synthesised by fusing MgO and Al_2O_3 with or without a mineraliser such as boric acid or water vapour.	
Talc	$Mg_3Si_4O_{10}(OH)_2$	no	It is formed during low-grade metamorphism of siliceous dolomites. Also by hydrothermal alteration of ultrabasic rocks.	1
Thendardite	Na_2SO_4	no	Occurs in playa-lake evaporites as in the alkali lakes.	
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	no	In thermally metamorphosed impure dolomites, tremolite forms early by reaction between dolomite and quartz.	1
Wollastonite	$CaSiO_3$	no	It is a product of high-grade thermal metamorphism of impure limestones. Also found in some alkaline igneous rocks.	5

Table A-1. A Modified Listing of Minerals from MINTEQA2 Online Handbook (Wadley and Buckley 1997) (Continued)

Mineral	Chemical Formula	Precipitates from 0-100 °C and at 1 ATM	Comments on Occurrence or Formation	Refs
Vivianite*	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	no	It is found with iron, copper and tin ones. It may occur in clay, and especially in bog iron-ore.	5
Wairakite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	no	It is found in sandstones and breccias.	5
Wustite	FeO	yes	Ferrous oxide is formed when ferric oxide is heated in hydrogen at 300. It also forms when ferrous oxalate is heated out of contact with the air.	7
ZnCl_2	ZnCl_2	yes	It is obtained by passing chlorine or hydrogen chloride over heated zinc.	2
$\text{Zn}(\text{OH})_2$	$\text{Zn}(\text{OH})_2$	yes	It is precipitated when an equivalent quantity of an alkaline hydroxide is added to solution of a zinc salt.	7
Zincite	ZnO	yes	It is formed by heating zinc in air and passing the fumes into condensing chambers where the powdered oxide collects.	7

1. Batley (1981); 2. Biquet (1963); 3. Dana and Ford (1922); 4. Deer, et al. (1966); 5. Gribble (1988); 6. Keith (1981); 7. Palache, et al. (1951); 8. Parkes (1961)